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AN EVALUATION OF ARSENITE PROCEDURE FOR DETERMINATION OF NITROGEN DIOXIDE IN AMBIENT AIR

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16. ABSTRACT

Report describes and evaluates the sodium arsenite manual procedure for measurement of NO_2 in ambient air. The evaluation included ruggedness testing, as described by Youden. The results showed a constant-high collection efficiency of 82 ±3.7% over the entire range. The method involves sampling for 24 hours with a restricted-orifice bubbler immersed in a $NaAsO_2$-NaOH collecting solution. The range of the method is approximately 20 to 750 ug/m^3. The method was insensitive to normal variations in orifice bubbler diameter, temperature of the absorbing solution during sampling, and concentration of arsenite. However, the ruggedness test identified NO and CO_2 as positive and negative interferents, respectively; sample flow rate may also be a variable affecting the method response.

An assessment of the usefulness of the method was deferred until the effects of the above interferents and of the flow rate have been quantitated.

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by

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CONTENTS

Section		Page
LIST OF TABLES		iv
LIST OF FIGURES		iv
I.	INTRODUCTION	1
II.	EXPERIMENTAL	2
III.	RESULTS AND DISCUSSION	6
IV.	CONCLUSIONS	21
V.	FUTURE WORK	21
VI.	REFERENCES	22
VII.	APPENDICES	25
TECHNICAL REPORT DATA SHEET		40

LIST OF TABLES

Table		Page
1.	Effect of Nitric Oxide on Collection Efficiency.	9
2.	Eight Combinations of Seven Factors Used to Test the Ruggedness of an Analytical Method	14
3.	Arsenite Method Ruggedness Test - Format	18
4.	Summary of Ruggedness Test Evaluation.	20

LIST OF FIGURES

Figure		Page
1	Percent Collection Efficiency of the Arsenite Method As a Function of NO_2 Concentration.	7
A-1	Sampling Train.	35
A-2	Flowmeter	36

AN EVALUATION OF ARSENITE PROCEDURE FOR DETERMINATION OF NITROGEN DIOXIDE IN AMBIENT AIR

I. INTRODUCTION

The Environmental Protection Agency (EPA) promulgated an annual average of 100 micrograms-per-cubic meter ($\mu g/m^3$) of nitrogen dioxide (NO_2) as a national primary ambient air quality standard. The standard and a 24-hour reference method for determining compliance were published in the Federal Register on April 30, 1971.[1] The reference method was later found to have a variable collection efficiency and a positive interference from nitric oxide (NO).[2,3,4] These deficiencies were considered serious and led EPA to search for new methods for measuring NO_2 in ambient air.

Christie et al.[5] reported a 95% collection efficiency of NO_2 in sodium hydroxide solutions containing 0.1% sodium arsenite. This method was investigated and adapted for field use by the Analytical Laboratory Branch (ALB) of the Quality Assurance and Environmental Monitoring Laboratory (QAEML) of EPA. ALB's preliminary investigation showed the arsenite (Christie) method to have a collection efficiency of 85%.[6] Thus, the arsenite method overcame the major deficiency of the original reference method and was chosen as one of three candidate reference methods published in the Federal Register as replacements for the original reference method.[7]

Investigation of the arsenite method was continued in order to establish its reliability. This report contains the results of an

evaluation of the method made by the Methods Standardization Branch (MSB) of QAEML. MSB is responsible for standardizing methods used in determining compliance with the national ambient air quality standards. This standardization process includes: 1) a review of the method write-up to insure that it is clearly written and technically accurate and, 2) a laboratory evaluation to determine if the method will perform according to the specifications of the write-up. The laboratory evaluation may include investigation or verification of such factors as stoichiometry, collection efficiency, concentration range or effect of interferents. The extent of the evaluation depends on how well the method has been developed and documented.

If a method proves to be reliable after MSB's evaluation, it can be subjected to a collaborative test designed to determine its precision (repeatability and reproducibility) and its accuracy (bias). The collaborative test is the final phase of the standardization process and is a measure of the performance of the method in actual use.

II. EXPERIMENTAL

A. General

The method used for the preliminary phase of this evaluation is described in the Federal Register.[7] The information gained in the preliminary evaluation was used to modify the original method write-up. The modified procedure was used as the basis for the final evaluation and is given in Appendix A. Basically, the method consists of drawing ambient air through a tube having a restricted orifice immersed in 50 ml

of a solution containing 0.1 N NaOH and 0.1% w/w sodium arsenite. The NO_2 in the ambient air is converted to nitrite ion. The concentration of nitrite ion is determined colorimetrically by formation of a purple azo-dye.

B. Sampling

Samples were collected in quintuplicate by attaching 5 sampling tubes to a common manifold. The flow rate for each tube was measured before and after sample collection as directed in the method. The total flow rate into the common manifold was also measured immediately before and after sampling and was compared with the sum of the individual flows to insure that there were no leaks in the system. Samples with a final flow more than 10% different from the initial flow were rejected.

C. Flow Control

The samples were collected at a rate of approximately 200cm^3/min by using a 27 gauge hypodermic needle as a critical orifice as suggested by the method. A Gast Model 0211 oil-less vacuum pump was used to maintain a pressure drop across the orifice of approximately 0.6-0.7 atmospheres. The total sampling time ranged from 20 to 24-hours.

D. Analysis

After sampling was completed, the tubes were disconnected from the manifold. Water lost by evaporation during the sampling was replaced and an aliquot of the sample was analyzed as described in the method. A Beckman Model "B" Spectrophotometer was used for the absorbance measurements.

E. Test Atmosphere Generation

1. Nitrogen Dioxide

Test atmospheres containing known amounts of NO_2 were generated by diluting the effluent from a gravimetrically calibrated NO_2 permeation device with various measured amounts of purified air. This procedure has been described by O'Keefe and Ortman,[8] and Scaringelli et al.[9, 10] The permeation device was made by the Microchemical Analysis Section of the National Bureau of Standards (NBS) and was calibrated frequently at intervals between sampling periods. The stability of permeation rates from these devices with respect to time has been well established.[11]

The temperature of the device was controlled by a water jacketed condenser, which was maintained at 25.0 ± 0.1°C by a Forma Temp, Jr. constant temperature bath. The NO_2 was flushed from the jacket by a flow of 100 cm^3/min dry N_2. The permeation rate for the device was 1.184 ± 0.001 µg/min. (Based on 66 weighings).

Purified air was obtained by passing compressed (House) air through silica gel for drying, treating with ozone to convert any NO to NO_2, and finally by passing through activated charcoal (6-A mesh), molecular sieve (6-16 mesh, type 4A), and silica gel (6-16 mesh) to remove any NO_2 and hydrocarbons.

2. Nitric Oxide

NO was introduced to the test atmospheres by means of a "T" connection in the NO_2 system. A Kjeldahl trap following the "T" insured mixing of the NO with the test atmosphere. A cylinder of NO in N_2 was analyzed by gas-phase titration with O_3 as described in the

Federal Register[7] and found to contain 100 ppm NO(122,700 $\mu g/m^3$) and 3.0 ppm NO_2(5644 $\mu g/m^3$). Because of the NO_2 "impurity" in the NO cylinder, it was necessary to calculate the exact NO_2 and NO concentrations using:

$$\frac{\text{P.R. } \mu g/\text{min}}{\text{X L/min}} \times \frac{10^3 \text{L}}{\text{m}^3} + \frac{\text{Y}}{\text{X}} \; 5644 \; \mu g \; NO_2/m^3 = \mu g \; NO_2/m^3$$

and $\frac{\text{Y L/min}}{\text{X L/min}}$ (122,700 μg NO/m^3) = μg NO/m^3

where

P.R. = permeation rate of NO_2 device

X = total dilution air flow rate

Y = NO flow rate

For test atmospheres containing a 4:1 ratio of $NO:NO_2$ approximately 80% of the NO_2 was from the permeation tube and 20% from the NO_2 impurity in the NO cylinder. For the atmospheres containing a 1:1 $NO:NO_2$ ratio 95% of the NO_2 was from the permeation tube and 5% from the NO cylinder.

3. Carbon Dioxide

CO_2 was added to the test atmosphere by means of a "T" connection, as in the addition of NO (see 2). The CO_2 was supplied from one of two cylinders containing 1060 ppm CO_2 in N_2 and 99.9% CO_2. Each cylinder was checked and found to be free of NO and NO_2 impurities by means of a chemiluminescent $NO\text{-}NO_2\text{-}NO_x$ monitor. The CO_2 concentration in each test atmosphere was calculated using:

$$\frac{F_{CO_2}}{F_{total}} \times C_{CO_2} = C'_{CO_2}$$

where F_{co_2} = flowrate from CO_2 cylinder

F_{total} = combined flow rates in manifold

C_{co_2} = concentration of CO_2 in cylinder

C'_{co_2} = concentration of CO_2 added to test atmosphere.

No attempt was made to control the CO_2 concentration in the purified air. Thus, the final CO_2 concentration was the ambient concentration, plus the amount added from the cylinder.

III. RESULTS AND DISCUSSION

A. Collection Efficiency

The preliminary evaluation of the arsenite method began with an investigation of the collection efficiency. Establishing the collection efficiency was essential because the original reference method had shown a 50% non-linear variation in collection efficiency over the concentration range[2] of the method and the arsenite method was only a modification of the original method.

The collection efficiency was determined by sampling test atmospheres containing 43.6[a], 77.7, 105, 106, 329, 449, 470, 644, and 743 µg NO_2/m^3. The samples were collected and analyzed according to the procedure described in the Federal Register.[7] Collection efficiencies (percent) were calculated by the ratio of NO_2 recovered (as nitrite ion) to NO_2 generated x 100 and are shown as a function of NO_2 concentration in Figure 1. Data for this figure is found in Appendix B. The least squares regression equation for the data is:

$$\% \text{ CE} = 82.46 - 0.00085 \ (\mu g NO_2/m^3)$$

The intercept of the equation (82.46) represents the collection efficiency of the method and the slope (-.00085) shows no significant change in

[a] An NO_2-permeation device with a rate of 0.723 µg/min was used to obtain this level.

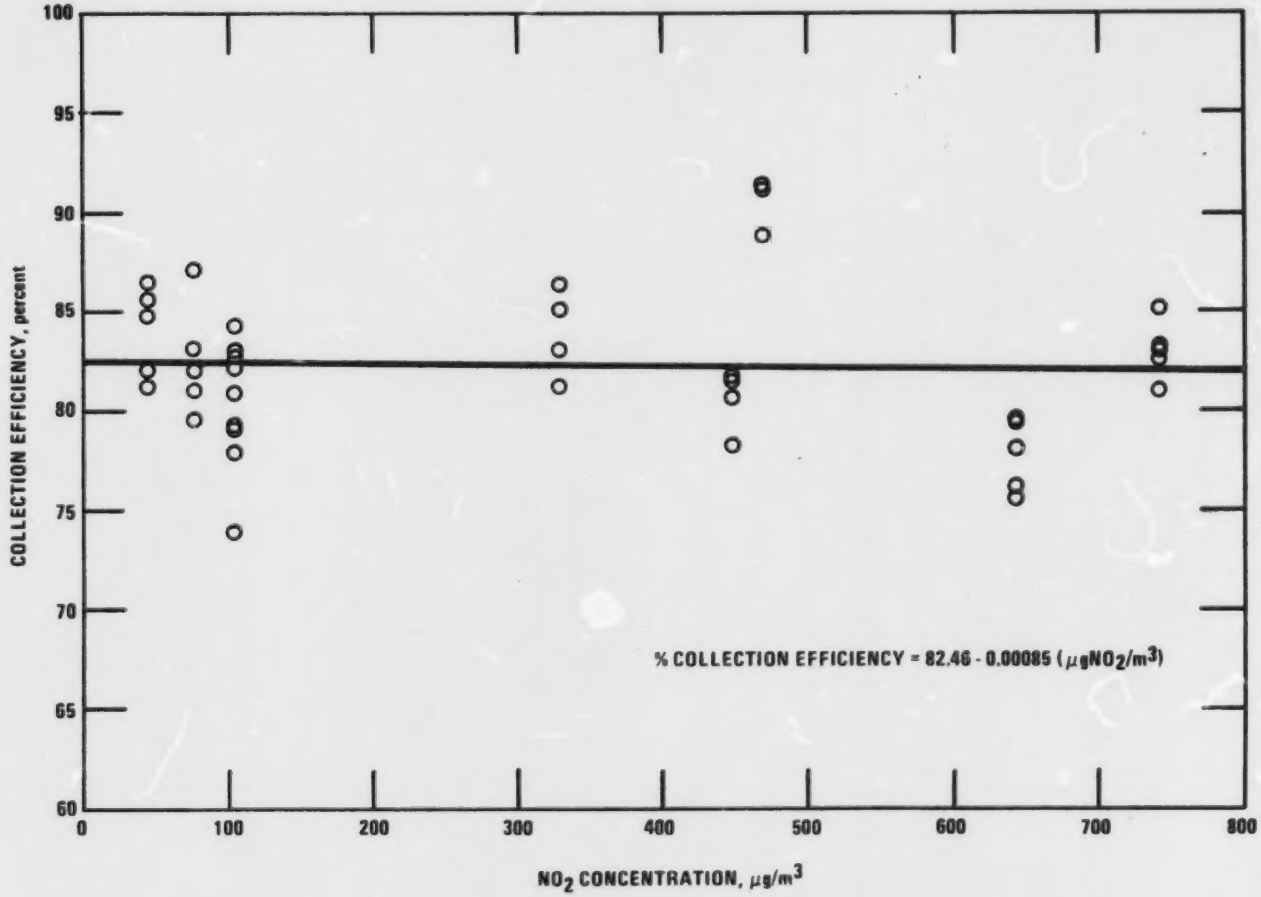

Figure 1. Percent collection efficiency of the arsenite method as a function of NO_2 concentration.

collection efficiency over the concentration range examined.

The arithmetic mean of the collection efficiencies obtained from the data in Appendix B is 82.2% with a relative standard deviation (RSD) of 4.5%. This is similar to the variability of other impinger collection systems.[9] More importantly, the data verifies that the variable collection efficiency of the original reference method has indeed been overcome by the arsenite modification.

B. Nitric Oxide Effect

The next step in the evaluation of the arsenite method was an investigation of the response of the method to nitric oxide (NO). The original reference method had shown an appreciable positive interference from NO.[2,3,4] The mechanism by which the NC interfere is believed to be described by the reaction

$$NO + NO_2 + 2^-OH \rightarrow 2NO_2^- + H_2O$$

In this reaction the NO interference depends on both the NO and NO_2 concentrations; therefore, it was necessary to sample test atmospheres containing various ratios of $NO:NO_2$ in order to evaluate their effect on the method.

Test atmospheres containing approximately 100 $\mu gNO_2/m^3$ and $NO:NO_2$ ratios (w/w) of 0:1, 1:1 and 4:1 were generated and sampled according to the method described in the Federal Register.[7] Collection efficiencies were calculated as in III.A. and are shown in Table 1.

Table 1. Effect of Nitric Oxide on Collection Efficiency.

$NO:NO_2$*	Mean Collection Efficiency	Standard Deviation
w/w	%	%
0:1	78.1	2.7
0:1	82.6	1.3
1:1	90.5	1.0
1:1	82.2	1.5
4:1	89.2	1.4
4:1	85.1	1.0

*NO_2 concentration 103 to 106 $\mu g NO_2/m^3$.

The atmospheres which contained only NO_2 (0:1) gave collection efficiencies of 78.1% and 82.6% (average 80.4 $\pm$ 3.2) and were used as a basis for comparison to measure the effect of the atmospheres containing NO. The test atmospheres containing a 1:1 ratio gave collection efficiencies of 90.5% and 82.2% (average 86.4 $\pm$ 5.9). By comparing the 1:1 values with the 0:1 values, it is difficult to draw any conclusions because of the variability of the data.

The 4:1 ratios gave values of 89.2% and 85.1% (average 87.2 $\pm$ 2.9). Comparing the base value (0:1) of 80.4 $\pm$ 3.2 with the 4:1 value of 87.2 $\pm$ 2.9, the effect of the NO becomes significant. However, the difference is small.

Additional work is needed to define the actual effect of NO in the arsenite method. However, it is important to note that the effect of the NO in the arsenite method is not as severe as that of the original reference method indicated by Hauser and Shy.[2]

C. Other Factors Evaluated

1. Orifice Diameter

The normal value for the diameter of the glass orifice in the bubbler was originally 0.4 mm. One lot of glass orifices supplied by a local glass blowing shop were examined and found to range from 0.4 mm to 0.9 mm. No significant difference in collection efficiency was found using orifice diameters between 0.4 and 0.8 mm. Therefore, the middle value and the range of orifices tested, 0.6 $\pm$ 0.2 mm, was adopted in place of 0.4 mm.

Pressure drops across the glass orifice in the sampler were between 10 and 16 mm Hg for the orifice diameters used. These pressure drops should have had no significant effect on the pressure drop across the critical orifice used for flow control.

2. Analytical System

The diazotation-coupling reaction used to detect nitrite in this analysis is well documented in the literature. However, certain parameters in the analysis were deemed worthy of investigation to insure that the arsenite modification had not affected them.

The optimum pH and time for color development were investigated and found to be 2.0 and 10 minutes, respectively. The color was stable for at least 30 minutes after development.

The stability of a collected NO_2 sample was investigated by analyzing a sample containing approximately 0.55 μg NO_2^-/ml (equivalent to 100 μg NO_2/m^3) at 0, 1, 4 and 41 days after collected. No significant change in concentration was found.

Since the pH, time for color development, and sample stability were found to be as described by the method and related litereature, no changes in the original specifications were necessary.

D. Preliminary Assessment

At this point in the investigation, a preliminary assessment of the arsenite method was made. The constant collection efficiency and lower response to NO overcame the most serious problems associated with the original reference method. Therefore, it was decided that a

further, more detailed, evaluation was warranted. The original method write-up, used in the preliminary experiments, was edited and modified to its present form (Appendix A) incorporating the information gained in the preliminary studies. This version of the method was then subjected to further investigation to determine the effect of various parameters which had not previously been evaluated.

E. Ruggedness Testing

1. Design

The second phase of the evaluation involved a test designed to determine the sensitivity of important operational parameters to slight changes similar to those encountered in normal use. This type of evaluation is called ruggedness testing. It is accomplished by conducting a series of controlled experiments in which selected parameters are varied at two levels: the nominal level stated in the method write-up and a challenging level. The results obtained using the nominal procedure are compared with the results obtained using the variation in order to determine the effect of the variable. Parameters which significantly effect the method response can then be more carefully controlled, thereby improving the method.

An ingenious scheme for determining the individual effects of variations in several parameters with a minimum number of experiments has been described by Youden.[12] Seven [a] parameters are

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[a] Schemes for examining the effect of a larger or smaller number of parameters are available.[13]

chosen for testing and their nominal values are denoted by A, B, C, D, E, F, and G. A challenging value for these parameters is then selected and denoted by a, b, c, d, e, f, and g. A series of eight experiments are then conducted using various combinations of either nominal or challenging values for each variable. The format for these experiments is shown in Table 2.

Each of the eight experiments produces a result, denoted as S, T, U, V, W, X, Y, and Z. Examination of the format in Table 2 reveals that by summing the group of experiment results in which a given nominal value was involved and subtracting from it the sum of the group of results in which the corresponding challenging value was involved, the effect of all other variables are canceled. If the grouped results are divided by the number in each group, the above subtraction will yield the average effect or difference between the nominal and challenging conditions.

For example, the average effect of variable A is calculated using

$$A\text{-}a = \frac{S+T+U+V}{4} - \frac{W+X+Y+Z}{4}$$

A complete set of equations for calculating the effect of A-a, B-b, etc. are given in Appendix C.

It should be noted that the results of the ruggedness test will not completely describe the effect of varying a given parameter. The results only show the effect of the range of variation used

Table 2. Eight Combinations of Seven Factors Used to Test the Ruggedness of an Analytical Method

Factor Value	Determination Number 1	2	3	4	5	6	7	8
A or a	A	A	A	A	a	a	a	a
B or b	B	B	b	b	B	B	b	b
C or c	C	c	C	c	C	c	C	c
D or d	D	D	d	d	d	d	D	D
E or e	E	e	E	e	e	E	e	E
F or f	F	f	f	F	F	f	f	F
G or g	G	g	g	G	g	G	G	g
Observed Result	S	T	U	V	W	X	Y	Z

in the experiment. If the effect is shown by the test to be significant, a series of tests controlling various levels of that parameter are then necessary to describe the exact relationship.

2. Selection of Parameters

Several parameters were considered to be subject to variation and possibly critical to the performance of the arsenite method.

a. Concentration

The effect of various concentrations of NO_2 on the arsenite method had been previously evaluated in the determination of the collection efficiency. However, the effect of other variables in association with the NO_2 concentration was not known. Therefore, NO_2 concentrations of 65 and 700 $\mu gNO_2/m^3$ were chosen to cover the range of the method.

b. Temperature

Methods used in the field are always subjected to extremes of temperature that can affect the collection efficiency of the method. The sampling devices used in most NO_2 networks are equipped with warming devices to eliminate the cold or near freezing temperatures. Therefore, a temperature of 25°C was selected for the nominal condition and 35°C was chosen for the challenge.

c. Orifice Size

Orifice size can affect collection efficiency by controlling the surface area of the bubbles produced in the solution. A test of the effect of an orifice diameter outside the prescribed 0.6 $\pm$ 0.2 mm was made by using 0.6 mm for the nominal value and 1.0mm for the

challenging value.

d. Flow Rate

The method requires a flow rate of 180 to 220 cm^3/min. Since the collection efficiency of a method can be affected by the rate of delivery of the sample to the absorbing solution, it was decided to examine the effect of flow rates. The nominal and challenging flows selected were 180 to 220 and 310 to 340 cm^3/min, respectively.

e. Sodium Arsenite Concentration

The original work by Christie determined the optimum amount of $NaAsO_2$ for NO_2 absorption by adding gaseous NO_2 to solutions containing various amounts of $NaAsO_2$ and then shaking the mixture.[5] Since this experiment does not duplicate the dynamic solution process of the sampling system, it was decided to examine $NaAsO_2$ concentration. The nominal value was 1.0g/L, as described in the method, and the challenging value was set at 0.8g/L.

f. Carbon Dioxide Concentration

Merryman reported a decrease in collection efficiency of an arsenite-type procedure with a CO_2 concentration of 2000 ppm.[4] However, he showed no effect with CO_2 near the ambient level of 300 ppm. Thus, a test to determine the effect of CO_2 concentrations slightly above the ambient level was conducted. The nominal value for CO_2 was the existing ambient concentration. The challenging concentration used was the nominal value, plus 300 ppm.

g. System Blank

The format described by Youden provides for evaluation of seven variables. If the performance of the method is well documented and understood, a complete set of seven variables may be tested. When the method does not meet these requirements, it is advisable to replace one of the variables with a system blank. It should be noted here that the system blank is unlike the customary blank in which the concentration of NO_2 would be zero. The system blank is merely a mathematical balance of all the variable conditions in the experiment.[12] If this experiment yields a low difference we may conclude that there were no uncontrolled factors which are critical to the performance of the method. Thus, a system blank was chosen for the seventh and final experiment in the ruggedness test.

3. Conducting the Ruggedness Test

a. Test Plan and Results

The parameters chosen for the ruggedness test were incorporated into the format previously described and are shown in Table 3. The experiments were conducted in random order (6, 1, 3, 7, 8, 2, 5, and 4) and the individual and average results for each determination are given in Appendix D. It should be noted that the results are expressed in per cent. This was calculated by dividing the concentration found by the concentration of NO_2 generated. This normalization of the results was necessary before the effect of the different parameters could be determined because, the method is obviously

Table 3. Arsenite Method Ruggedness Test Format

Factor Value	Determination Number 1	2	3	4	5	6	7	8
NO_2 Concentration A = 65μg/m^3 a = 700μg/m^3	65μg/m^3	65	65	65	700	700	700	700
Absorber Temperature B = 25°C b = 35°C	25°C	25	35	35	25	25	35	35
Orifice Size C = 0.6mm c = 1.0mm	0.6mm	1.0	0.6	1.0	0.6	1.0	0.6	1.0
Flow Rate D = 200cm^3/min d = 300cm^3/min	200cm^3/min	200	300	300	300	300	200	200
Sodium Arsenite Conc. E = 1.0g/L e = 0.8g/L	1.0g/L	0.8	1.0	0.8	0.8	1.0	0.8	1.0
CO_2 Concentration F = Ambient f = Ambient+300	Ambient	Amb. + 300	Amb.+300	Ambient	Ambient	Amb.+300	Amb.+300	Ambient
System Blank G = g, No variation	-	-	-	-	-	-	-	-
Observed Result	S	T	U	V	W	X	Y	Z

sensitive to NO_2 concentration.

The results in Appendix D were substituted into the equations of Appendix C and the effect of each parameter was calculated. The net results are shown ranked in order of absolute magnitude in Table 4.

b. Results

1. Carbon Dioxide Concentration

The most significant effect on the arsenite method was due to the CO_2 concentration. The positive value of 18.3% indicates that the recovery of NO_2 is significantly reduced by the presence of an additional 300 ppm CO_2 (over ambient) in the air sample. Thus, CO_2 is a negative interferent in the method.

2. Flow Rate

The recovery of NO_2 was apparently reduced by 14.4% by flow rates of 300 cm^3/min instead of the 200 cm^3/min required by the method. However, this effect may be related to the increased CO_2 intake at the higher flow rate rather than the flow rate alone.

3. Orifice Size

The negative 2.6% value obtained for this variable indicates the 1.0mm orifice has a slightly greater recovery than the 0.6mm orifice. The preliminary evaluation of this variable indicated that increasing the orifice size had the reverse of this result, although the magnitude did not appear to be significant. The small magnitude of this result and the possible contradiction between

Table 4. Summary of Ruggedness Test Evaluation.

Rank	Factors	Difference %
1.	CO_2 Concentration Ambient vs Ambient + 300	18.3
2.	Flow Rate $\sim 200 cm^3/min$ vs $\sim 300 cm^3/min$	14.4
3.	Orifice Size 0.6mm vs 1.0mm	(-) 2.6
4.	NO_2 Concentration $65 \mu g/m^3$ vs 700 $\mu g/m^3$	(-) 1.9
5.	$NaAsO_2$ Concentration 1.0g/L vs 0.8g/L	(-) 1.5
6.	Temperature 25°C vs 35°C	1.2
7.	Experiment Blank	1.1

the preliminary evaluation and the ruggedness test are considered to be of no consequence.

4. Other Parameters

The values obtained for the NO_2 concentration, $NaAsO_2$ concentration, temperature, and system blank were 1.9, -1.5, 1.2 and 1.1%, respectively. These values indicate that the effects of these variations were insignificant. The small difference obtained for the system blank indicates that there were no critical factors uncontrolled in the test.

IV. CONCLUSIONS

The arsenite method has a constant-high collection efficiency over the entire range of the method. The method is insensitive to normal variations in: orifice bubbler diameter, temperature of the absorbing solution during sampling, and concentration of sodium arsenite. However, NO and CO_2 are positive and negative interferents, respectively; sample flow rate may also be a variable affecting the method response and should be closely controlled.

Before an assessment can be made as to the utility of the arsenite method for measuring NO_2 in ambient air, the effect of the above interferents, and flow rate, on the method response needs to be quantiated. (Present-incomplete data indicate that the interference from NO is small, approximately 10%).

V. FUTURE WORK

Future work will involve determining if the reduced method response attributed to flow rate, as a result of the ruggedness test, was caused by increasing the NO_2 sampling rate and/or CO_2 consumption.

Additional combinations of NO plus NO_2 and CO_2 plus NO_2 will be sampled to quantify the effect of these interferents on the method response. The experiments will be designed so that equations can be developed from the data that will allow calculation of the effect of NO or CO_2 concentration (in combination with NO_2) on the method response.

This information will allow a judgment to be made as to the practical magnitude of the interferences and consequently the utility of the method for making NO_2 measurements. If both the interferences are minimal, the method could be used as is and the fact documented with the equations. If either of the interferences is too high, further development of the method to eliminate the interference(s) would be recommended.

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VII. Appendices

A. Tentative Method for the Determination of Nitrogen Dioxide in the Atmosphere (Sodium Arsenite Procedure).*

B. Collection Efficiency vs Concentration.

C. Equations for Evaluation of the Ruggedness Test.

D. Arsenite Method Ruggedness Test Data.

*A tentative method is one that has been carefully drafted from available experimental information, reviewed editorially within the Methods Standardization Branch, and undergone extensive laboratory evaluation. The method is still under investigation and, therefore, is subject to revision.

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APPENDIX A. TENTATIVE METHOD FOR THE DETERMINATION OF NITROGEN DIOXIDE IN THE ATMOSPHERE (SODIUM ARSENITE PROCEDURE)

1. Principle and Applicability

1.1 Nitrogen dioxide is collected by bubbling air through a sodium hydroxide-sodium arsenite[1] solution to form a stable solution of sodium nitrite. The nitrite ion produced during sampling is reacted with phosphoric acid, sulfanilamide, and N-1-(naphthyl)ethylenediamine dihydrochloride to form an azo dye and then determined colorimetrically.

1.2 The method is applicable to collection of 24-hour samples in the field and subsequent analysis in the laboratory.

2. Range and Sensitivity

2.1 The range of the analysis is 0.04 to 2.0 μg NO_2^-/ml. Beer's law is obeyed through this range (0 to 1.0 absorbance units). With 50 ml absorbing reagent and a sampling rate of 200 cm^3/min for 24-hours, the range of the method is 20 to 750 $\mu g/m^3$ (0.01 to 0.4 ppm) nitrogen dioxide.[2]

2.2 A concentration of 0.04 μg NO_2^-/ml will produce an absorbance of approximately 0.02 with 1-cm cells.

3. Interferences

3.1 Nitric oxide is a positive interferent.[3] The presence of NO can increase the NO_2 response by 5 to 15% of the NO_2 sampled.[2]

3.2 The interference of sulfur dioxide is eliminated by converting it to sulfate ion with hydrogen peroxide before analysis.[4]

4. Precision, Accuracy and Stability

4.1 The relative standard deviations for sampling NO_2 concentrations of 78, 105 and 329 $\mu g/m^3$ are 3, 4 and 2%, respectively.

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4.2 No accuracy data are available.

4.3 Collected samples are stable for at least 6 weeks.

5. Apparatus

5.1 Sampling. A diagram of a suggested sampling apparatus is shown in Figure 1.

5.1.1 Probe. Teflon, polypropylene, or glass tube with a polypropylene or glass funnel at the end.

5.1.2 Absorption Tube. Polypropylene tubes 164 x 32 mm, equipped with polypropylene two-port closures. Rubber stoppers cause high and varying blank values and should not be used. A glass-tube restricted orifice is used to disperse the gas. The tube, approximately 8 mm O.D.-6 mm I.D., should be 152 mm long with the end drawn out to 0.3 - 0.8 mm I.D.[a] The tube should be positioned so as to allow a clearance of 6 mm from the bottom of the absorber.

5.1.3 Moisture Trap. Polypropylene tube equipped with two-port closure. The entrance port of the closure is fitted with tubing that extends to the bottom of the trap. The unit is loosely packed with glass wool to prevent moisture entrainment.

5.1.4 Membrane Filter. Of 0.8 to 2.0 microns porosity.

5.1.5 Flow Control Device. Any device capable of maintaining a constant flow through the sampling solution between 180-220 cm^3/min. A typical flow control device is a 27 gauge hypodermic needle,[5] three-eights inch long. (Most 27 gauge needles will give flow rates in this range.) The device used should be protected from particulate matter. A membrane filter is

[a] This specification was modified after the completion of our study by additional information obtained from other investigators.

suggested. Change filter after collecting 10 samples.

5.1.6 Air Pump. Capable of maintaining a pressure differential of at least 0.6-0.7 of an atmosphere across the flow control device. This value includes the minimum useful differential, 0.53[5] atmospheres, plus a safety factor to allow for variations in atmospheric pressure.

5.1.7 Calibration Equipment. - Flowmeter for measuring airflows up to 275 cm^3/min. within $\pm$ 2%, stopwatch, and a precision wet test meter (1 liter/revolution).

5.2 Analysis

5.2.1 Volumetric Flasks. 50, 100, 200, 250, 500, 1,000 ml.

5.2.2 Graduated Cylinder. 1,000 ml.

5.2.3 Pipets. 1, 2, 5, 10, 15 ml volumetric; 2 ml, graduated in 1/10 ml intervals.

5.2.4 Test Tubes, approximately 20 x 150 mm.

5.2.5 Spectrophotometer. Capable of measuring absorbance at 540 nm.

6. Reagents

6.1 Sampling

6.1.1 Sodium Hydroxide. ACS Reagent Grade.

6.1.2 Sodium Arsenite. ACS Reagent Grade.

6.1.3 Absorbing Reagent. Dissolve 4.0 g sodium hydroxide in distilled water, add 1.0 g of sodium arsenite and dilute to 1,000 ml with distilled water.

6.2 Analysis

6.2.1 Sulfanilamide. Melting point, 165-167°C.

6.2.2 N-(1-Naphthyl)-ethylenediamine dihydrochloride (NEDA). Best grade available.

6.2.3 Hydrogen Peroxide. ACS Reagent Grade, 30%.

6.2.4 Sodium Nitrite. Assay of 97% $NaNO_2$ or greater.

6.2.5 Phosphoric Acid. ACS Reagent Grade, 85%.

6.2.6 Sulfanilamide Solution. Dissolve 20 g sulfanilamide in 700 ml distilled water. Add, with mixing, 50 ml concentrated phosphoric acid and dilute to 1,000 ml. This solution is stable for one month, if refrigerated.

6.2.7 NEDA Solution. Dissolve 0.5 g of NEDA in 500 ml of distilled water. This solution is stable for one month, if refrigerated and protected from light.

6.2.8 Hydrogen Peroxide Solution. Dilute 0.2 ml of 30% hydrogen peroxide to 250 ml with distilled water. This solution may be used for one month, if protected from light and refrigerated.

6.2.9 Standard Nitrite Solution. Dissolve sufficient desiccated sodium nitrite and dilute with distilled water to 1,000 ml so that a solution containing 1,000 µg NO_2^-/ml is obtained. The amount of $NaNO_2$ to use is calculated as follows:

$$G = \frac{1.500}{A} \times 100$$

G = Amount of $NaNO_2$ grams.

1.500 = Gravimetric factor in converting NO_2 into $NaNO_2$.

A = Assay, percent.

7. Procedure

7.1 Sampling. Assemble the sampling apparatus as shown in Figure 1. Components upstream from the absorption tube may be connected, where required, with teflon or polypropylene tubing; glass tubing with dry ball joints; or glass tubing with butt-to-butt joints with tygon, teflon or polypropylene. Add exactly 50 ml of absorbing reagent to the calibrated absorption tube (8.1.3). Disconnect funnel, insert calibrated flowmeter, and measure flow before sampling. If flow rate before sampling is not between 180 and 220 cm^3/min, replace the flow control device and/or check the system for leaks. Start sampling only after obtaining an initial flow rate in this range. Sample for 24 hours and measure the flow after the sampling period.

7.2 Analysis. Replace any water lost by evaporation during sampling by adding distilled water up to the calibration mark on the absorption tube. Pipet 10 ml of the collected sample into a test tube. Pipet in 1 ml hydrogen peroxide solution, 10 ml sulfanilamide solution, and 1.4 ml NEDA solution with thorough mixing after the addition of each reagent. Prepare a blank in the same manner using 10 ml of unexposed absorbing reagent. After a 10-minute color-development interval, measure the absorbance at 540 nm against the blank. Read $\mu g\ NO_2^-$/ml from the calibration curve (Section 8.2). Samples with an absorbance greater than 1.0 must be reanalyzed after diluting an aliquot (less than 10 ml) of the collected sample with unexposed absorbing reagent.

8. Calibration and Efficiencies

8.1 Sampling

8.1.1 Calibration of Flowmeter. (See Figure 2). Using a wet test meter and a stopwatch, determine the rates of air flow (cm^3/min) through the flowmeter at a minimum of four different ball positions. Plot ball positions versus flow rates.

8.1.2 Flow Control Device. The flow control device results in a constant rate of air flow through the absorbing solution. The flow rate is determined in Section 7.1.

8.1.3 Calibration of Absorption Tube. Calibrate the polypropylene absorption tube (Section 5.1.1) by first pipeting in 50 ml of water or absorbing reagent. Scribe the level of the meniscus with a sharp object, go over the area with a felt-tip marking pen, and rub off the excess.

8.2 Calibration Curve. Dilute 5.0 ml of the 1,000 µg NO_2^-/ml solution to 200 ml with absorbing reagent. This solution contains 25 µg NO_2^-/ml. Pipet 1, 1, 2, 15, and 20 ml of the 25 µg NO_2^-/ml solution into 100-, 50-, 50-, 250-, and 250- ml volumetric flasks and dilute to the mark with absorbing reagent. The solutions contain 0.25, 0.50, 1.00, 1.50 and 2.00 µg NO_2^-/ml, respectively. Run standards as instructed in 7.2, including the blank. Plot absorbance vs. µg NO_2^-/ml. A straight line with a slope of 0.48 $\pm$ 0.02 absorbance units/µg NO_2^-/ml, passing through the origin, should be obtained.

8.3 Efficiencies. An overall average efficiency of 82% was obtained over the range of 40 to 750 $\mu g/m^3$ NO_2.

9. Calculation

9.1 Sampling

9.1.1 Calculate volume of air sampled.

$$V = \frac{F_1 + F_2}{2} \times T \times 10^{-6}$$

V = Volume of air sampled, m^3.

F_1 = Measured flow rate before sampling, cm^3/min.

F_2 = Measured flow rate after sampling, cm^3/min.

T = Time of sampling, min.

10^{-6} = Conversion of cm^3 to m^3.

9.1.2 Uncorrected Volume. The volume of air sampled is not corrected to S.T.P. because of the uncertainity associated with 24-hour average temperature and pressure values.

9.2 Calculate the concentration of nitrogen dioxide as μg NO_2/m^3 using:

$$\mu g\ NO_2/m^3 = \frac{(\mu g\ NO_2^-/ml) \times 50}{V \times 0.82}$$

50 = Volume of absorbing reagent used in sampling, ml.

V = Volume of air sampled, m^3.

0.82 = Collection efficiency.

9.2.1 If desired, concentration of nitrogen dioxide may be calculated as p.p.m. NO_2 using:

$$p.p.m.\ NO_2 = (\mu g\ NO_2/m^3) \times 5.32 \times 10^{-4}$$

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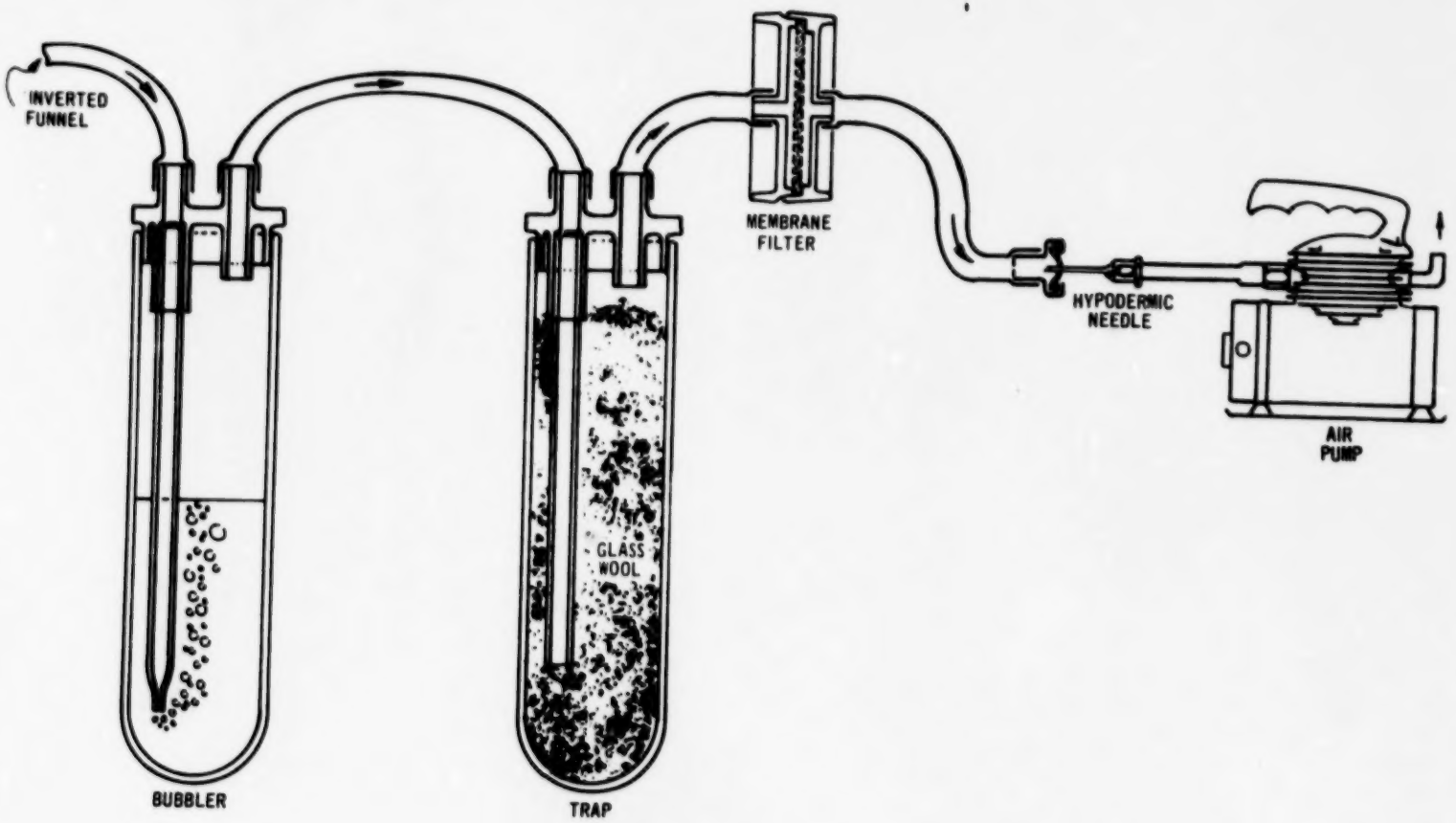

Figure A-1. Sampling train.

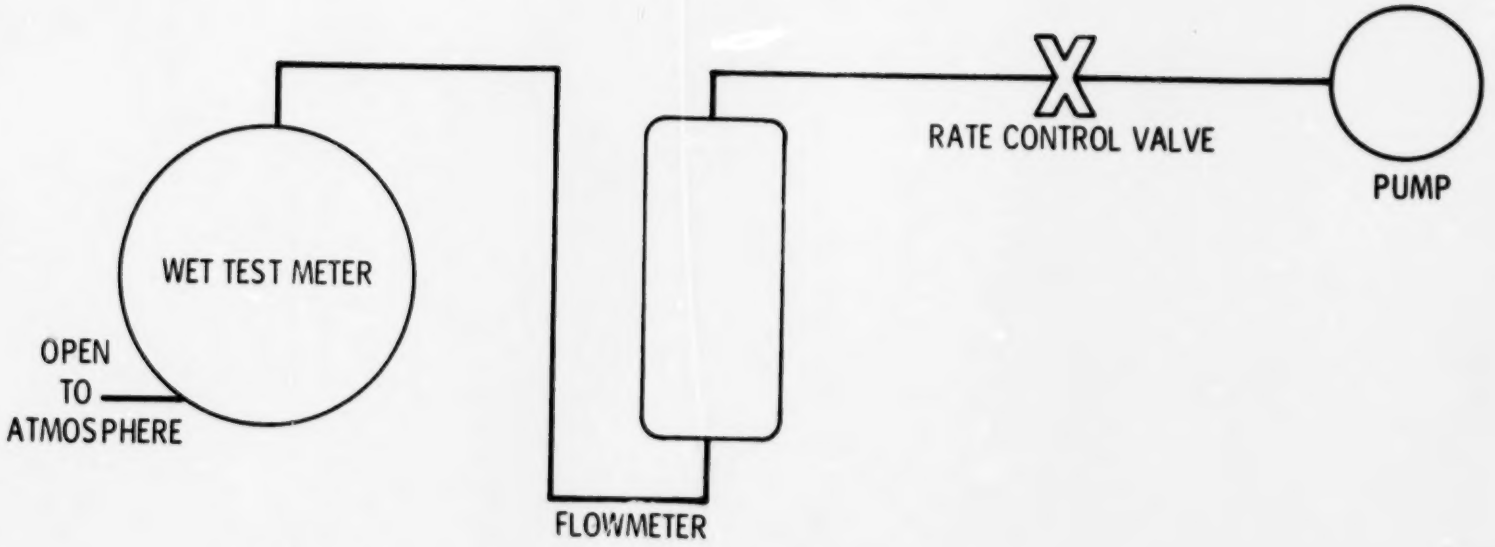

Figure A-2. Flowmeter.

Appendix B. Collection Efficiency vs Concentration.

NO_2 Generated $\mu g/m^3$	NO_2 Found $\mu g/m^3$	Collection Efficiency	Mean %	Standard Deviation %
	37.3	85.6		
	37.0	84.9		
43.6	35.8	82.1	84.1	2.3
	35.4	81.2		
	37.7	86.5		
	61.8	79.5		
	62.9	81.0		
77.7	63.7	82.0	82.5	2.9
	64.6	83.1		
	67.7	87.1		
	77.5	73.8		
	84.8	80.8		
105	83.3	79.3	78.1	2.7
	83.1	79.1		
	81.8	77.9		
	88.1	83.1		
	89.3	84.2		
106	87.8	82.8	82.6	1.3
	85.7	80.8		
	87.0	82.1		
	280	85.1		
	280	85.1		
329	273	83.0	84.1	2.0
	284	86.3		
	267	81.2		
	366	81.5		
	367	81.7		
449	351	78.2	80.5	1.4
	362	80.6		
	362	80.6		
	429	91.3		
470	428	91.1	90.4	1.4
	417	88.7		
	511	79.3		
	502	78.0		
644	486	75.5	77.7	1.8
	512	79.5		
	490	76.1		
	632	85.1		
	616	82.9		
743	601	80.9	82.9	1.5
	613	82.5		
	617	83.0		

Appendix C. Equations for Evaluation of the Ruggedness Test.

1. $A\text{-}a = \frac{S + T + U + V}{4} - \frac{W + X + Y + Z}{4}$

2. $B\text{-}b = \frac{S + T + W + X}{4} - \frac{U + V + Y + Z}{4}$

3. $C\text{-}c = \frac{S + U + W + Y}{4} - \frac{T + V + X + Z}{4}$

4. $D\text{-}d = \frac{S + T + Y + Z}{4} - \frac{U + V + W + X}{4}$

5. $E\text{-}e = \frac{S + U + X + Z}{4} - \frac{T + V + W + Y}{4}$

6. $F\text{-}f = \frac{S + V + W + Z}{4} - \frac{T + U + X + Y}{4}$

7. $G\text{-}g = \frac{S + V + X + Y}{4} - \frac{T + U + W + Z}{4}$

Appendix D. Arsenite Method Ruggedness Test Data.

Determination No.	NO_2 Generated $\mu g/m^3$	NO_2 Found $\mu g/m^3$	% Response	Mean %	Observed Result Designation %
		61.8	93.8		
		62.8	95.3		
1	65.9	59.0	89.5	92.6	S
		63.2	95.9		
		58.4	88.6		
		48.4	72.7		
		52.0	78.1		
2	66.6	52.9	79.4	77.5	T
		52.0	78.1		
		52.6	79.0		
		36.2	54.5		
		39.5	59.5		
3	66.4	38.0	57.2	57.8	U
		39.3	59.2		
		39.0	58.7		
		53.5	80.7		
		54.6	82.4		
4	66.3	54.1	81.6	81.1	V
		53.5	80.7		
		53.2	80.2		
		617	83.8		
		593	80.6		
5	736	596	81.0	80.5	W
		595	80.8		
		560	76.1		
		485	66.0		
		498	67.8		
6	735	478	65.0	64.7	X
		473	64.4		
		443	60.3		
		541	74.9		
		551	76.3		
7	722	551	76.3	76.7	Y
		549	76.0		
		576	79.8		
		696	93.9		
		707	95.4		
8	741	698	94.2	94.8	Z
		696	93.9		
		716	96.6		